FTA0407 6/11

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 013 151 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 79302994.3

(22) Date of filing: 20.12.79

(51) Int. Cl.³: B 01 D 53/14

(30) Priority: 22.12.78 US 972500

(43) Date of publication of application: 09.07.80 Bulletin 80/14

(84) Designated Contracting States: DE FR GB IT NL

(71) Applicant: Exxon Research and Engineering Company
P.O.Box 390 200 Park Avenue
Florham Park New Jersey 07932(US)

(72) Inventor: Say, Geoffrey Rhys
3020 Tall Timbers Road
Baton Rouge, Louisiana(US)

(72) Inventor: Hays Sr., James Richard
9878 Chateau Drive
Baton Rouge, Louisiana(SU)

(72) Inventor: Iyengar, Jagannathan Nambi
443 West Main Street
Rockaway, New Jersey(US)

(74) Representative: Somers, Harold Arnold et al.
5 Hanover Square
London W1R 9HE(GB)

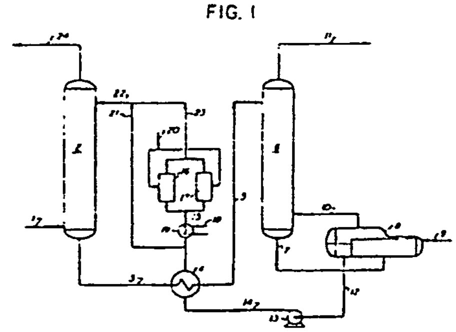
(54) Process for maintaining the performance of aqueous hindered amine scrubbing liquid in acid gas scrubbing.

(57) Acid gases such as CO_2 and H_2S are scrubbed from a gas mixture in an absorption zone (2) employing an aqueous solution (22) comprising an alkali metal compound and a sterically hindered amine of formula: R-NH_2-$(CH_2)_m$-NH_2 in which R is a secondary or tertiary alkyl or cycloalkyl C_4 to C_{20} hydrocarbon group and *m* is from 2 to 5, under elevated temperature and pressure causing the formation of a cyclic urea of formula:

$$\underline{\ulcorner (CH_2)_m\text{-}CH_2\text{-}NH\text{-}C(O)\text{-}N(R)\text{-}CH_2 \urcorner}$$

in which R is a secondary or tertiary C_4 to C_{20} alkyl or cycloalkyl hydrocarbon and *m* is from 0 to 3. The solution containing absorbed acid gases is steam stripped in a regeneration zone (6, 8) and a portion of the resulting lean solution is cooled (in 19) to a temperature at which the cyclic urea selectively precipitates. The cooled portion of the solution is passed through a filter (16 or 17) to separate the cyclic urea solids before being recirculated (23) with the rest (21) of the lean solution to the absorption zone (2).

FIG. 1



EP 0 013 151 A1

Croydon Printing Company Ltd

Exxon Research and Engineering Company

Process for Maintaining the Performance of Aqueous Hindered Amine Scrubbing Liquid in Acid Gas Scrubbing

The present invention relates to a process for maintaining the performance of an aqueous hindered amine scrubbing liquid used in acid gas scrubbing, and more particularly, to a process for the removal of a cyclic urea reaction product in an amine gas treating process which involves an absorption and a regeneration system. Still more particularly, the invention is concerned with the selective precipitation and filtration of a cyclic urea degradation product which forms as a by-product in the feed gas scrubbing process.

It is well known in the art to treat gases and liquids, such as mixtures containing acidic gases including CO_2, H_2S, SO_2, SO_3, CS_2, HCN, COS and oxygen and sulfur derivatives of C_1 - C_4 hydrocarbons with amine solutions to remove these acidic gases. The amine usually contacts the acidic gases and liquids as an aqueous solution containing the amine in an absorber tower with the aqueous amine solution contacting the acidic fluid countercurrently.

The acidic scrubbing processes known in the art can be generally classified into three (3) categories.

The first category is generally referred to as the aqueous amine process where relatively large amounts of amine solution are employed during the absorption. This type of process is often utilized in the manufacture of H_2 for ammonia production where nearly complete removal of the acid gas, such as CO_2 is required. It is also used in those instances where an acid gas, such as CO_2 occurs with other acid gases or where the partial pressure of the CO_2 and other gases is low.

The second category is generally referred to as the aqueous base scrubbing process or "hot potash" process. In this type of process a small level of an amine is included as an activator for the aqueous base used in the scrubbing solution. This type of process is generally used where bulk removal of an acid gas, such as CO_2 is desired. This process also applies to situations where the CO_2 and feed gas pressures are high. In such processes, useful results are achieved using aqueous potassium carbonate solutions as amine activators.

A third category is generally referred to as the non-aqueous solvents process. In this process, water is a minor constituent of the scrubbing solution and the amine is dissolved in the liquid phase containing the solvent. In this process up to 50% of amine is dissolved in the liquid phase. This type of process is utilized for specialized applications where the partial pressure of CO_2 is extremely high and/or where many acid gases are present, e.g., COS, CH_3SH, and CS_2.

The present invention relates to a process for the selective separation of a cyclic urea degradation product which may form as a by-product of the practice of the second category of acid scrubbing process described above, namely, the aqueous base scrubbing process or "hot potash" process in which a hindered amine is used.

Many industrial processes for removal of acid gases, such as CO_2, use regenerable aqueous alkali scrubbing solutions, such as an amine and potassium carbonate which are continuously circulated between an absorption zone where acid gases are absorbed and a regeneration zone where they are desorbed, usually by steam-stripping. The capital cost of these acid scrubbing processes is generally controlled by the size of the absorption and regeneration towers, the size of the reboilers for generating stripping steam, and the size of the condensers, which condense spent stripping steam so that condensate may be returned to the system to maintain proper water balance. The cost of operating such scrubbing

plants is generally related to the amount of heat required for the removal of a given amount of acid gas, e.g., thermal efficiency, sometimes expressed as cubic feet of acid gas removed per pound of steam consumed. Means for reducing the costs in operating these industrial processes have focused on the use of absorbing systems or combinations of chemical absorbants which will operate more efficiently and effectively in acid gas scrubbing processes using existing equipment.

It is disclosed in U.S. Patent Nos. 4,112,050; 4,112,051 and 4,112,052 that sterically hindered amines unexpectedly improve the efficiency, effectiveness and cyclic working capacity of the acid gas scrubbing processes in all three of the above-mentioned process categories. In the case of the sterically hindered amine activated "hot potash" CO_2 containing acid gas scrubbing process of the invention described in U.S. Patent No. 4,112,050, the process can be operated at a cyclic working capacity significantly greater than when diethanolamine or 1,6-hexanediamine is the amine activator used in a similar process. It is postulated that the increase in cyclic capacity observed with the sterically hindered amines is due to the instability of their carbamates. In that respect, sterically hindered amines are similar to tertiary amines. Tertiary amines are not used on a commercial scale for carbon dioxide containing acid gas scrubbing due to their low rates of absorption and desorption.

N-alkyl alkylene diamines are advantageously used as sterically hindered amine activators in the "hot pot" process. A preferred sterically hindered amine used as an activator in the "hot pot" process is N-cyclohexyl-1,3-propanediamine. This amine in the presence of an amino acid is sufficiently water soluble under absorption and desorption conditions to maintain a single phase and it also has a very high absorption capacity.

Although N-cyclohexyl-1,3-propane diamine has been found to produce excellent results as an activator in the "hot pot" treating process, one drawback in processes where it has

been used is that it produces a cyclic urea product when the acid treated gas is rich with CO_2 and also contains H_2S. The cyclic urea has a deleterious effect on CO_2 removal rates and must be removed and replaced with fresh N-cyclohexyl-1,3-propanediamine. The makeup rate for the hindered amine has a minimal effect on the process economics; however, the cyclic urea that is formed must be selectively removed in order to be able to maintain acid gas removal performance.

The invention which is disclosed herein represents an improvement to the "hot pot" amine activated gas treating process which includes the use of a hindered amine having a tendency to form cyclic ureas under CO_2 rich conditions in the presence of H_2S. This invention discloses a processing step wherein the cyclic urea can be selectively removed from the circulating solution thereby preventing any loss in acid gas removal capabilities.

SUMMARY OF THE INVENTION

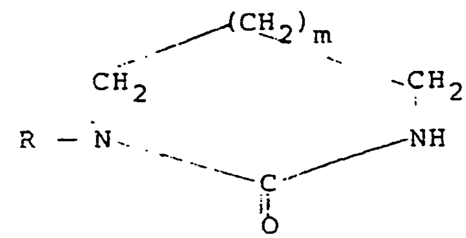
An acid gas scrubbing process providing for the selective separation of a cyclic urea reaction product which forms as a by-product during the acid gas removal, said process comprising:

(a) contacting an acid gas mixture with an aqueous solution, preferably in countercurrent flow, in an absorption zone, said aqueous solution comprising an alkaline material comprised of a basic alkali salt or metal hydroxide selected from the group consisting of alkali metal bicarbonates, carbonates, hydroxides, borates, phosphates and their mixtures, and an activator for said basic salt comprising at least one sterically hindered amine having the generic formula:

$$R\text{-}NH\text{-}(CH_2)_m\text{-}NH_2$$

where R is a secondary or tertiary alkyl or cycloalkyl hydrocarbon having 4-20 carbon atoms and m is 2-5, at elevated temperatures and pressures such that a cyclic urea degradation product having the generic formula:

BAD ORIGINAL



where R is a secondary or tertiary alkyl or cycloalkyl having 4-20 carbon atoms and m is 0-3; is formed and a loading of 1 to 10 SCF of acid gas per gallon of said aqueous solution is achieved;

(b) passing the acid gas rich aqueous solution produced from said step (a) to a regeneration zone operated at temperatures ranging from 200°F to 250°F and pressures ranging from 1 psig to 15 psig where it is contacted, preferably in countercurrent flow, with steam to strip the acid gas impurities therefrom;

(c) cooling a portion of the lean solution exiting from said regeneration zone to temperatures ranging from 80-180°F such that said cyclic urea degradation product is selectively precipitated from said lean solution;

(d) passing said lean solution containing said precipitated cyclic urea degradation product to a separation zone to remove at least a portion of said cyclic urea degradation product from said lean solution.

In a preferred mode of operation, the invention comprises the additional steps of:

(e) monitoring the accumulation of said degradation product in said separation zone, preferably a filter medium, until the pressure drop across said filter medium reaches about 25 psi at which time said filter is segregated and a clean filter is substituted therefor;

(f) the segregated filter is cleaned by washing with hot water having a preferred temperature of 200°-240°F.

The degradation product forms primarily at rich conditions and gradually builds up in the solution causing a drop-off in acid gas removal capabilities for the circulat-

ing solution. When there is a buildup, it becomes necessary to remove the cyclic urea degradation product so as to maintain the enhanced acid gas removal rate for the hindered amine solution. This is accomplished in the process of the present invention by providing a slip stream from the lean solution which is cooled to a preferred temperature of 130°-160°F and then passed over a bed of carbon or a filter medium.

The cyclic urea material was found to have unanticipated solubility properties when present in the circulating solution which contains K_2CO_3, $KHCO_3$, KHS, the sterically hindered amine and amino acid. The cyclic urea which has certain physical properties similar to those of the hindered amine was found unexpectedly to selectively come out of the solution as it was cooled from 200°F to a temperature of about 180-80°F. The desired specific temperature may be chosen on the basis of the concentration of K_2CO_3 in the solution. In this connection a typical temperature operating range for various K_2CO_3 concentrations is given in Figure 2 described hereinafter.

For a scrubbing solution comprising about 30 wt.% K_2CO_3 and cooled to 160°- 130°F little or none of the other components come out of the solution. If this 30 wt.% K_2CO_3 solution is cooled to 100°F and below, then $KHCO_3$ will also precipitate from the solution and the process will no longer be selective. Similarly, for a solution comprising 25 wt.% K_2CO_3 and cooled to a temperature between 80° and 140°F only cyclic urea is precipitated from the solution.

The invention disclosed herein describes the temperature region in which the cyclic urea can be selectively precipitated and removed without removing any of the other many components in the solution.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow diagram of one embodiment of the claimed invention.

Figure 2 is a plot of the typical operating region in which cyclic urea can be selectively precipitated as a

function of wt.% K_2CO_3 in a solution and the solution temperature.

DETAILED DESCRIPTION OF THE INVENTION

The acidic components which will be removed from the gaseous mixture by the scrubbing process will preferably be selected from the group consisting of CO_2 alone or in combination with H_2S, SO_2, CS_2, HCN, COS and the oxygen and sulfur derivatives of C_1-C_4 hydrocarbons.

The alkaline material comprising basic alkali salts or metal hydroxides will be selected from the group consisting of alkali metal bicarbonates, carbonates, hydroxides, borates, phosphates and their mixtures.

The contacting of the absorbent mixture and the acid gas may take place in any suitable contacting tower. In such processes, the gaseous mixture from which the acid gases are to be removed may be brought into intimate contact with the absorbing solution using conventional control means such as a tower packed with, for example, ceramic rings or with bubble capped plates or sieve plates or a bubble reactor. In a preferred mode of practicing the invention, the absorption step is conducted by feeding the gaseous mixture into the base of the tower while the lean absorbing solution is fed into the top. The gaseous mixture, free largely from acid gases, emerges from the top. Preferably, the temperature of the absorbing solution during the absorption step is in the range from about 150°F to about 270°F and more preferably from 150°F to about 250°F. Pressures may vary widely, acceptable pressures being between 5 and 2000 psig. In the desorber, the pressures will range from about 1 to 15 psig. The process can be better understood by reference to the following detailed description.

Referring to the figure, sour gas is introduced via line 1 into absorption column 2 where it is contacted with the aqueous scrubbing solution introduced via line 22. The scrubbing solution is at a temperature of about 200°F and has an amine concentration of from 1 to 10 wt.%, preferably 3 to

8 wt.%. As the absorbent liquid passes down the absorber column, acid gas impurities are absorbed.

The absorbent solution, enriched with acid gas impurities, passes out of absorber column 2 into line 3 which passes the enriched solution through heat exchanger 4 into line 5. Line 5 passes the enriched solution into the regenerator 6 where the acid gases are stripped from the solution and pass overhead through line 11. The lean solution formed in the regenerator column passes to the bottom of column 6 and out via line 7 which feeds the lean solution to reboiler 8 where it is boiled by steam entering via line 9, the acid vapors being passed via line 10 to the regenerator 6. The lean (essentially acid free) solution passes out of reboiler 8 via line 12. Line 12 passes the lean solution through pump 13 into line 14. Line 14 passes the lean solution into heat exchanger 4 and some of the solution is cooled further in heat exchanger 19 with cooling water entering via line 18 down to cool the solution to the temperature range in which substantially only cyclic urea is precipitated. As used herein, the term "precipitate" is defined as particles which are separated from the solution irrespective of whether the particles would settle to the bottom of the solution or float on top. In this process the cyclic urea removed from the solution is less dense than the solution and hence will float on the surface. For a solution comprising about 30 wt.% K_2CO_3 the solution should be preferably cooled to 180°F to 120°F, as indicated in Figure 2, more preferably to 160° to 130°F, most preferably 150° to 135°F to selectively precipitate the cyclic urea degradation product while keeping all other components in the solution. Similarly, as shown in Figure 2, a 25 wt.% K_2CO_3 solution should be cooled to a temperature ranging between 80°F and 140°F, preferably 90°-120°F, to selectively precipitate only the cyclic urea. Maximum cooling effect for typical K_2CO_3 concentrations may be obtained by operation at a temperature in the range of between 120°F-80°F. The solution containing the cyclic urea

BAD ORIGINAL

solids is passed into line 15 which passes it to filter element 16. The cyclic urea degradation product accumulates on the filter and is thereby selectively removed from the lean solution. When the ultimate buildup of the insoluble material on the filter causes a pressure drop of, for example, about 25 psi, a secondary filter 17 is cut in to allow continued operation of the process during the cleaning of the segregated filter.

The lean solution passes out of filter 16 via line 23 and joins with some of the other lean solution in line 21 which was not cooled by exchanger 19. These two streams combine and enter the top of the absorber. The purified gas passes out of absorber 2 via line 24. Hot water having a temperature of about 230°F is passed via line 20 into filter element 16 in order to wash the cyclic urea from the filter and to permit its effective reuse.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following is a summary of several examples which describe the invention.

EXAMPLE 1

A gas treating solution was prepared which had the following composition: 30 wt.% K_2CO_3 (with 10% as $KHCO_3$). 6.0 wt.% cyclohexyl-1,3-propane diamine, 6.1 wt.% pipecolinic acid, 56.2 wt.% water, and 1.7 wt.% cyclic urea, i.e., 1-cyclohexyl-hexahydro-2-pyrimidinone. The solution at 200°F was present as a single liquid phase. This solution was then cooled at 150°F and was passed over a filter element which was a cotton wound element having a nominal 100u size. The cyclic urea content was decreased from 1.7 wt.% to less than 1.0 wt.%. The filtration rate was 0.5 gpm and the filter size was a 3" diameter cylinder, 4" high with an inner opening of about 1" diameter. The filter cake was analyzed to be pure cyclic urea with none of the other solution components present. This example shows that the cyclic urea can be selectively removed by this process. It is not necessary to completely remove all the cyclic urea but just to be able

to keep the concentration at a nominally low level [illegible] it is constantly being produced within the process.

EXAMPLE 2

The gas treating solution described in Example 1 was cooled to 130°F at which point considerably more cyclic urea came out of the solution. Operation of the process at these conditions, however, produced a somewhat inoperable condition due to the plugging tendency of the resulting precipitate. In the flowing system in which the stream is being continuously filtered such a line plugging tendency as observed above made the system somewhat inoperable. Therefore, this test indicated that for this solution cooling to below 130°F leads to an undesired operability problem. The solids which were filtered during the test were again found to be pure cyclic urea with none of the other components of the solution present.

EXAMPLE 3

Another gas treating solution was prepared that was similar to that shown in Example 1 but which had about 30% of the K_2CO_3 present as $KHCO_3$. In this solution, cooling from 200°F to 150°F again caused the cyclic urea to selectively precipitate from the solution. As the solution was further cooled to somewhat below 100°F, it was found that the process was no longer selective in that in addition to the cyclic urea precipitating out, $KHCO_3$ was also precipitated out. This test further shows the critical temperature range over which the cyclic urea selectively precipitates. If the temperature goes below about 100°F, the process is no longer selective. The filter cake in this test was found to contain substantial amounts of $KHCO_3$.

EXAMPLE 4

Another gas treating solution was prepared which had a composition similar to that shown in Example 1 except that the cyclic urea content was 1.4 wt.%. This solution was cooled to 148°F and was filtered using a filter arrangement as described in Example 1 but with a 5. element rather

than the 100μ element. The run was carried out at 0.5 gpm and the filter cake collected was analyzed and was found to be pure cyclic urea. In this test, the run was carried out until the pressure drop across the element reached about 25 psi.

EXAMPLE 5

After completion of the run described in Example 4 the filter had a pressure drop of 25 psi due to the cyclic urea cake on the filter element. This cake was washed with 170°F water and a second cycle was attempted in which case a run of only about 25% as long as the initial run occurred. This indicated that the washing with 170°F water was not an effective cleaning process. The filter was then washed with 230°F water and then another cycle was attempted. In this case, the cycle length was equivalent to that of the initial cycle on the fresh filter. Three more complete cycles were run in which the filter cake was washed with 230°F water after a 25 psi pressure drop had built up due to the accumulation of the cyclic urea cake. In each case the amount of cyclic urea removed was the same as that with a new filter. These tests indicated an effective washing technique in which the water temperature criticality was demonstrated.

EXAMPLE 6

Another gas treating solution was prepared comprising: 25 wt.% K_2CO_3 (with 20% of this present as $KHCO_3$), 6.3 wt.% cyclohexyl-1,3-propane diamine, 3 wt.% pipecolinic acid, 0.8 wt.% cyclic urea and the balance water. The solution was then cooled to about 85°F. The filter cake was collected, analyzed, and found to be substantially pure cyclic urea.

Although the subject process has been described with reference to a specific embodiment, it will be understood that it is capable of further modification. Any variations, uses or adaptations of the invention following, in general, the principles of the invention are intended to be covered, including such departures from the present disclosure as come within known or customary practice in the art to which the

[illegible] parts as or as may be applied to the essential features [illegible] and do fall within the [illegible] the invention.

[illegible]

Temperatures given in °F are converted to °C by subtracting 32 and then dividing by 1.8.

Volumes in cubic feet or standard cubic feet are converted to litres by multiplying by 28.32.

Volumes given in gallons or gallons per minute (gpm) are converted to litre equivalents by multiplying by 3.785.

Weights given in pounds (lbs) are converted to kilograms by multiplying by 0.45359.

Lengths given in inches (") are converted to centimetres by multiplying by 2.54.

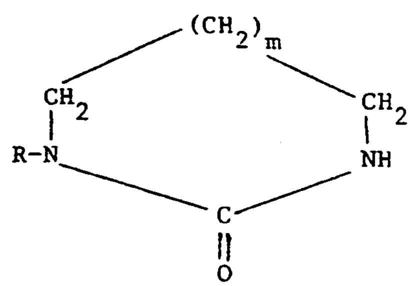
Pressures given in pounds per square inch (psi) or pounds per square inch gauge (psig) are converted to kg/cm^2 by multiplying by 0.07031.

CLAIMS:

1. An acid gas scrubbing process comprising contacting an acid gas mixture with an aqueous solution in an absorption zone (2), said aqueous solution comprising a basic alkali salt, or metal hydroxide selected from alkali metal bicarbonates, carbonates, hydroxides, borates, phosphates and their mixtures, and an activator for said basic salt comprising at least one sterically hindered amine having the generic formula:

$$R\text{-}NH\text{-}(CH_2)_m\text{-}NH_2$$

where R is a secondary or tertiary alkyl or cycloalkyl hydrocarbon having 4-20 carbon atoms and m is 2 - 5, thereby forming an acid gas-rich aqueous solution, and passing the said acid gas-rich aqueous solution (via line 3) to a regeneration zone (6, 8) wherein the acid gas-rich solution is contacted with steam (via line 9) to remove acid gas therefrom (via line 11) to form a lean solution, characterized by operating the process at such conditions of elevated temperature and pressure that there is formed a cyclic urea reaction product having the formula:



where R is a secondary or tertiary alkyl or cycloalkyl hydrocarbon having 4 - 20 carbon atoms and m is 0 - 3; cooling (in 19) a portion of the lean solution exiting from said regeneration zone (6, 8) to a temperature in the range of from 180-80^{o}F (82.3 to 26.7^{o}C) to selectively precipitate the cyclic urea from said lean solution; and passing said lean solution containing said precipitated cyclic urea to a separation zone (16, 17) to remove at least a portion of the cyclic urea from said lean solution.

2. A process according to claim 1 characterized in that the said sterically hindered amine is an N-alkyl alkylene diamine, preferably cyclohexyl 1-1,3-propane diamine.

3. A process according to claim 1 or claim 2 characterized in that the said lean solution exiting from said regeneration zone (6, 8) is cooled (in 19) to a temperature in the range of from 130° - 160°F (54.5 to 71.2°C).

4. A process according to claim 1 or claim 2 characterized in that the said lean solution exiting from said regeneration zone (6, 8) is cooled (in 19) to a temperature in the range of from 90-120°F (31 to 49°C).

5. A process according to any one of claims 1-4 characterized in that the said cyclic urea is removed by passing said lean solution through separation media (16, 17) comprising porous filters or activated carbon beds.

6. A process according to claim 5 characterized in that the accumulation of said cyclic urea on said filter (16, 17) is monitored until the pressure drop across said filter (e.g. 16) reaches about 25 psi at which time said filter (16) is segregated to interrupt the passage of lean solution therethrough and a second filter (17) is substituted therefor and lean solution caused to pass through the second filter (17).

7. A process according to any one of claims 1 to 6 characterized in that the portion of lean solution from which cyclic urea has been separated is recirculated to the absorption zone (2).

8. A process according to any one of claims 1 to 7 characterized in that lean solution other than said portion thereof is recirculated back to the absorption zone (2)

BAD ORIGINAL

FIG. 1

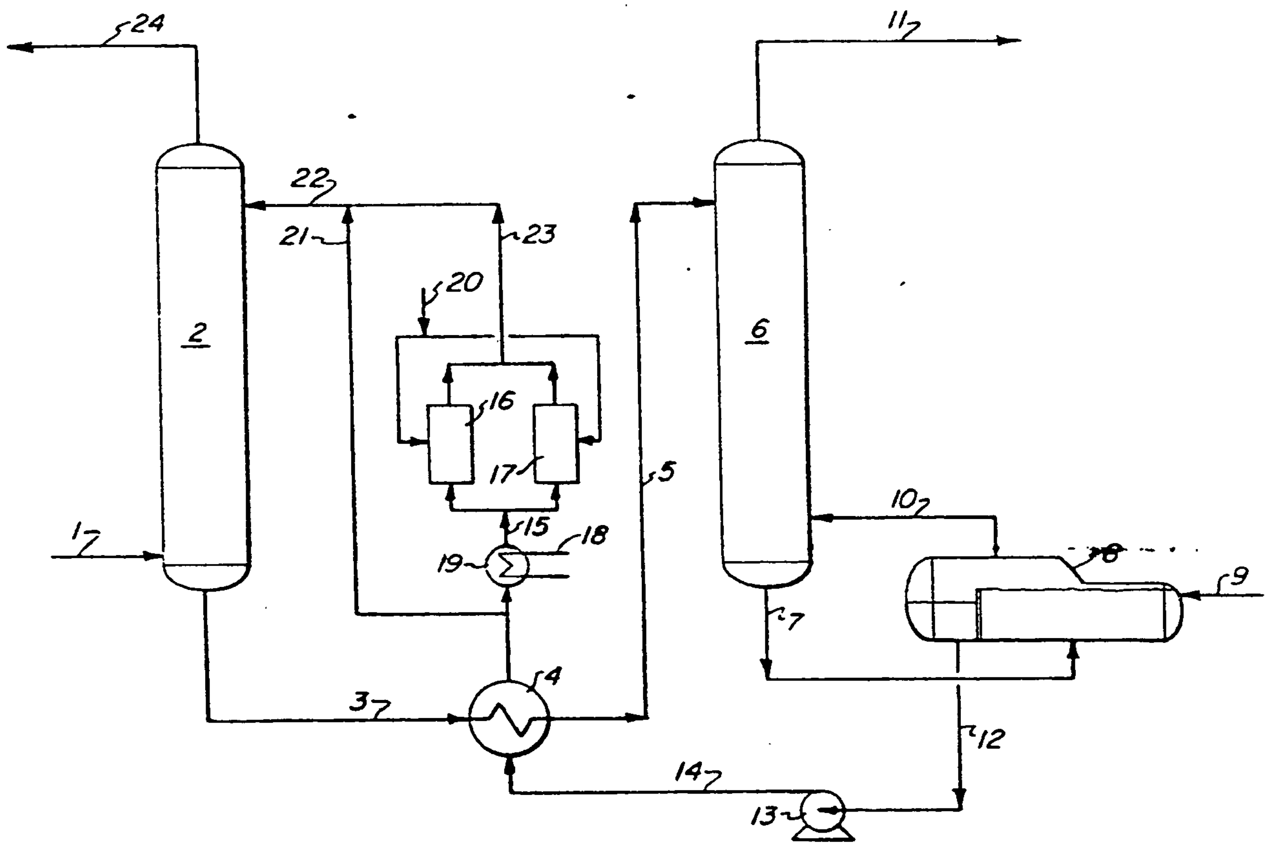
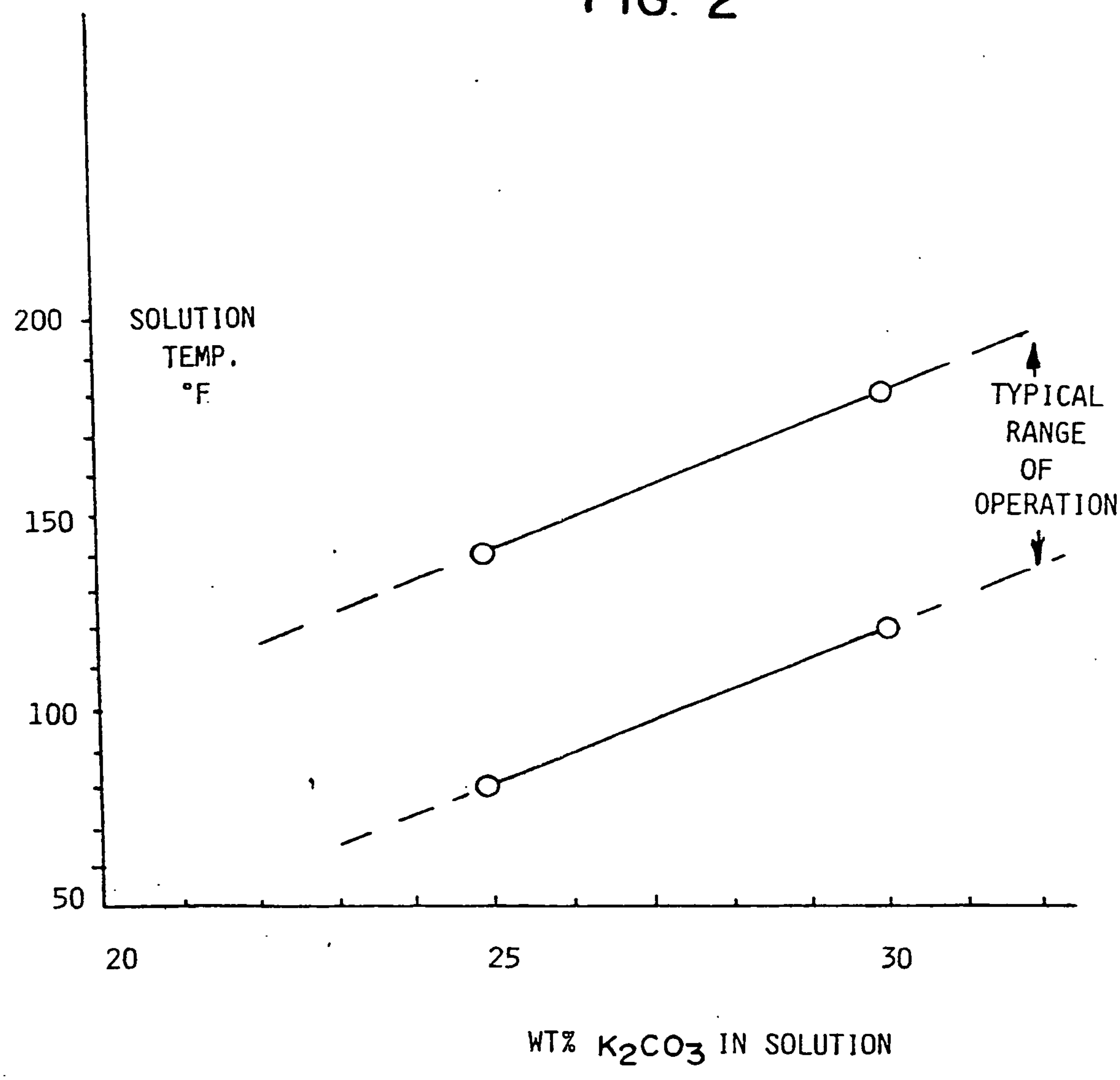


FIG. 2


200
150
100
50
SOLUTION
TEMP.
°F
TYPICAL
RANGE
OF
OPERATION
20
25
30
WT% K_2CO_3 IN SOLUTION

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 79 30 2994

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	GB - A - 1 449 039 (TRENTHAM CORP.)	
A	FR - A - 2 374 071 (EXXON)	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

B 01 D 53/14

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

B 01 D 53/00
C 10 K 1/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	25-03-1980	BOGAERTS